

Figure 1

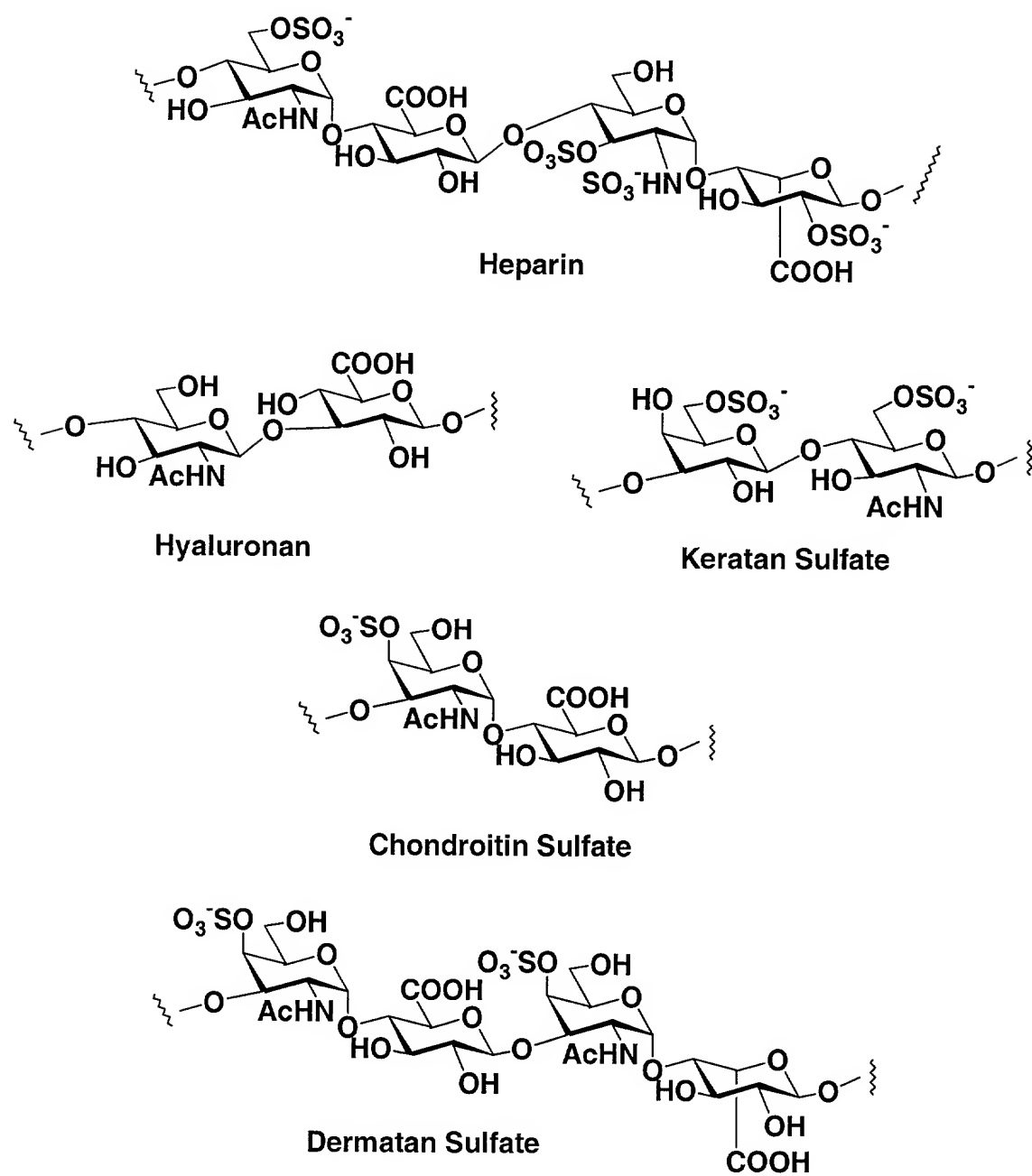


Figure 2

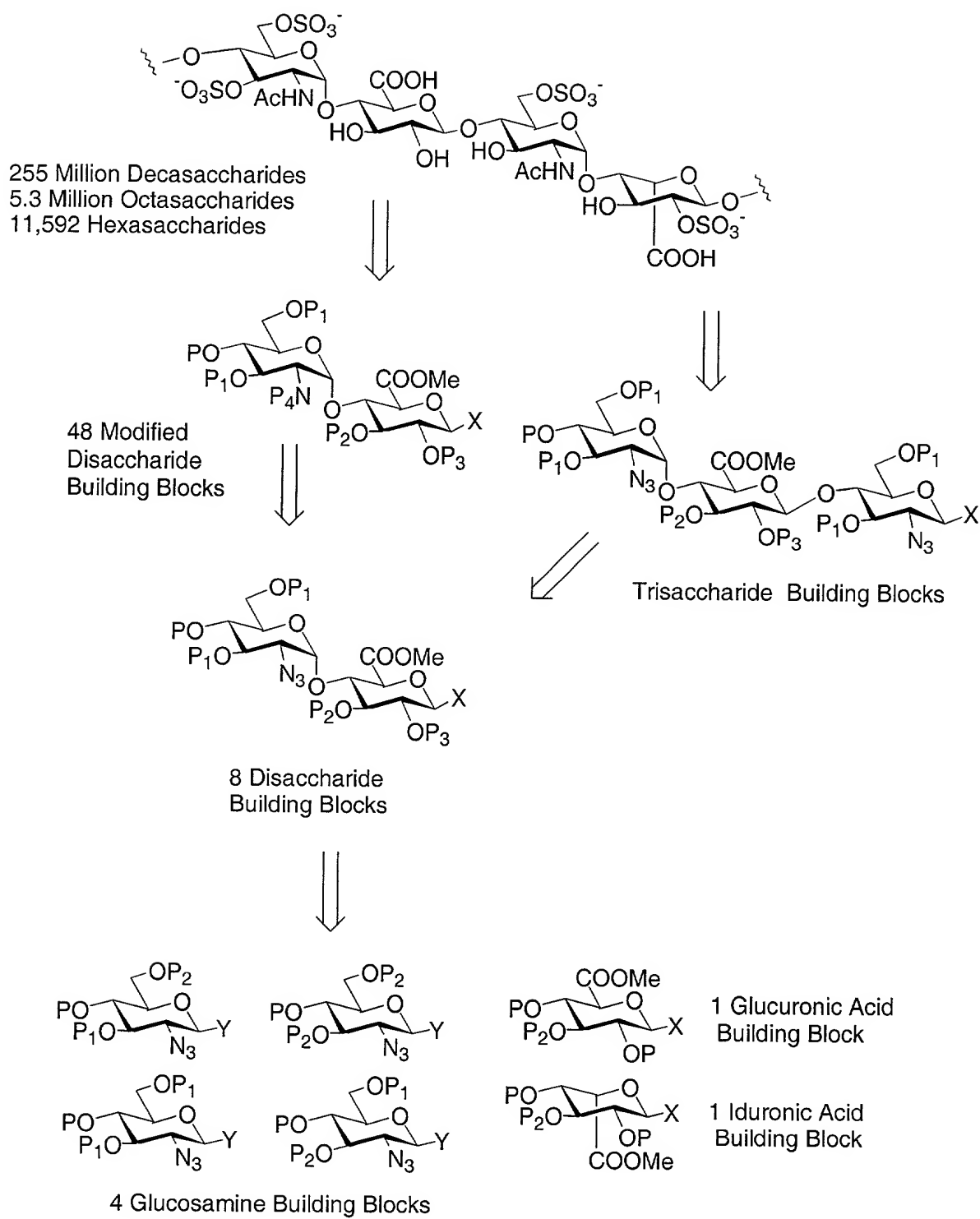
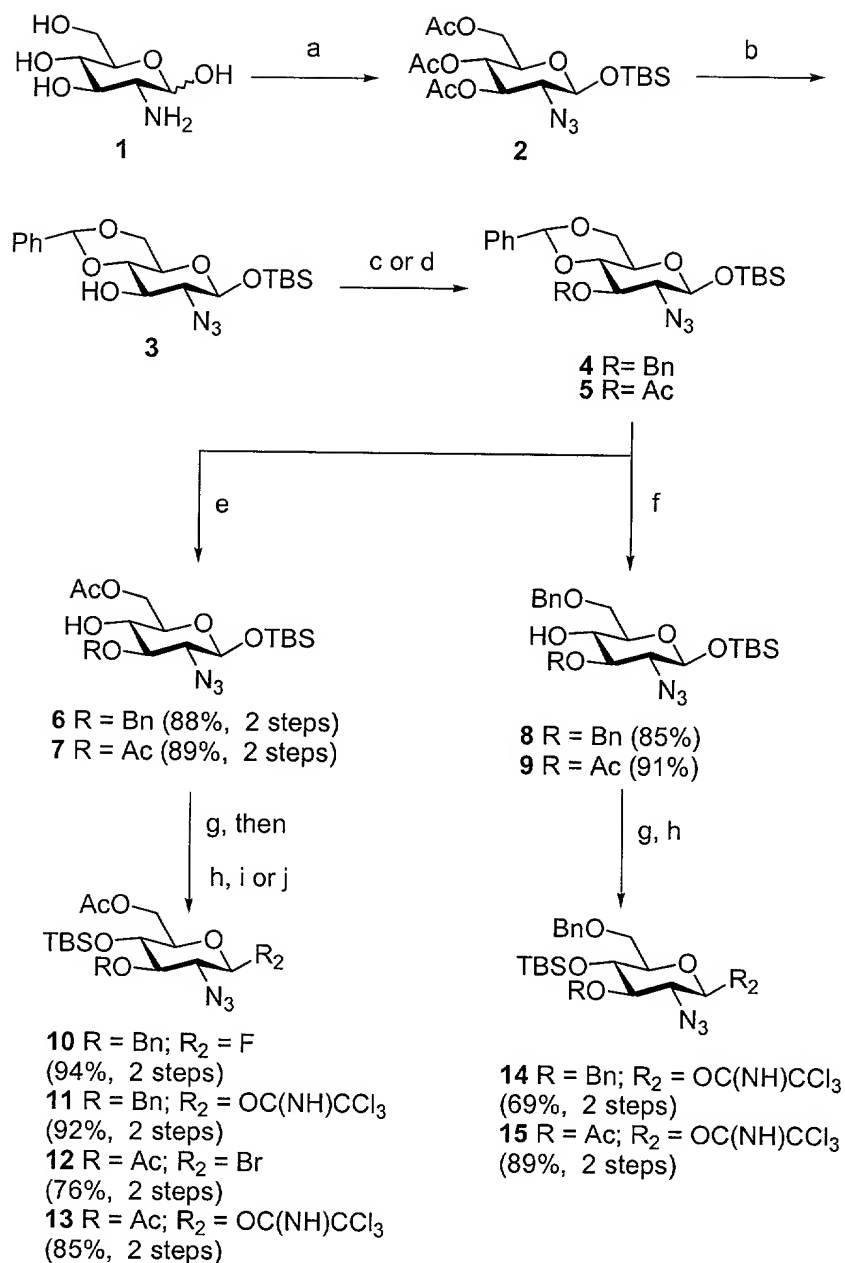
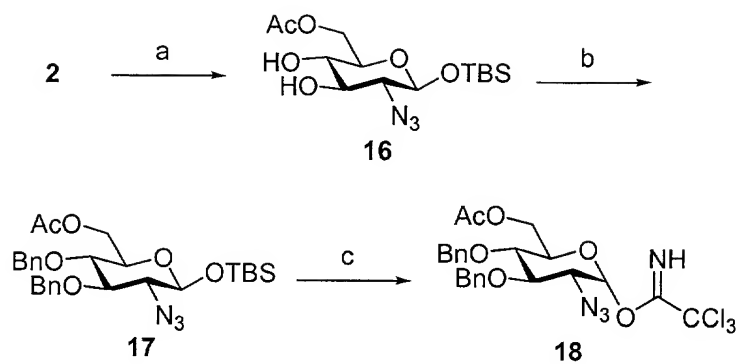


Figure 3



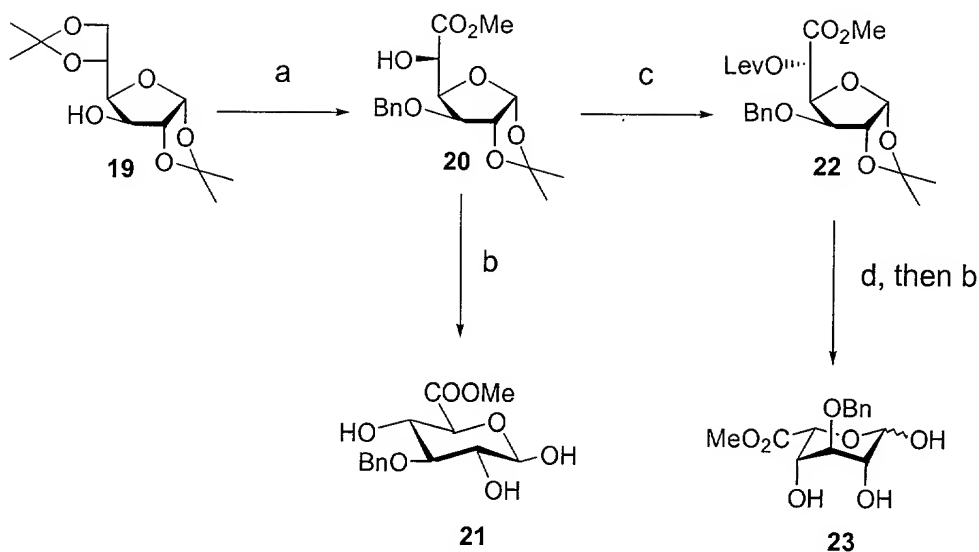
- a) 1. TfN₃, H₂O, K₂CO₃, CH₂Cl₂, MeOH, CuSO₄; 2. Ac₂O, pyridine, DMAP;
 3. NH₃, MeOH, THF; 4. TBSCl, imidazole, CH₂Cl₂, 72% (four steps);
 b) 1. NaOMe, MeOH; 2. PhCH(OMe)₂, pTsOH, CH₃CN, 86% (two steps);
 c) BnBr, Ag₂O, 4Å molecular sieves, CH₂Cl₂, 95%; d) Ac₂O, DMAP, pyridine;
 e) 1. TFA (60% aq.), CH₂Cl₂; 2. AcCl, collidine, -40°C; f) TES, TFA, CH₂Cl₂;
 g) 1. TBSOTf, lutidine, CH₂Cl₂; 2. TBAF, AcOH, THF; h) CCl₃CN, DBU, CH₂Cl₂;
 i) DAST, CH₂Cl₂, 0°C; j) SOBr₂, imidazole, THF.

Figure 4



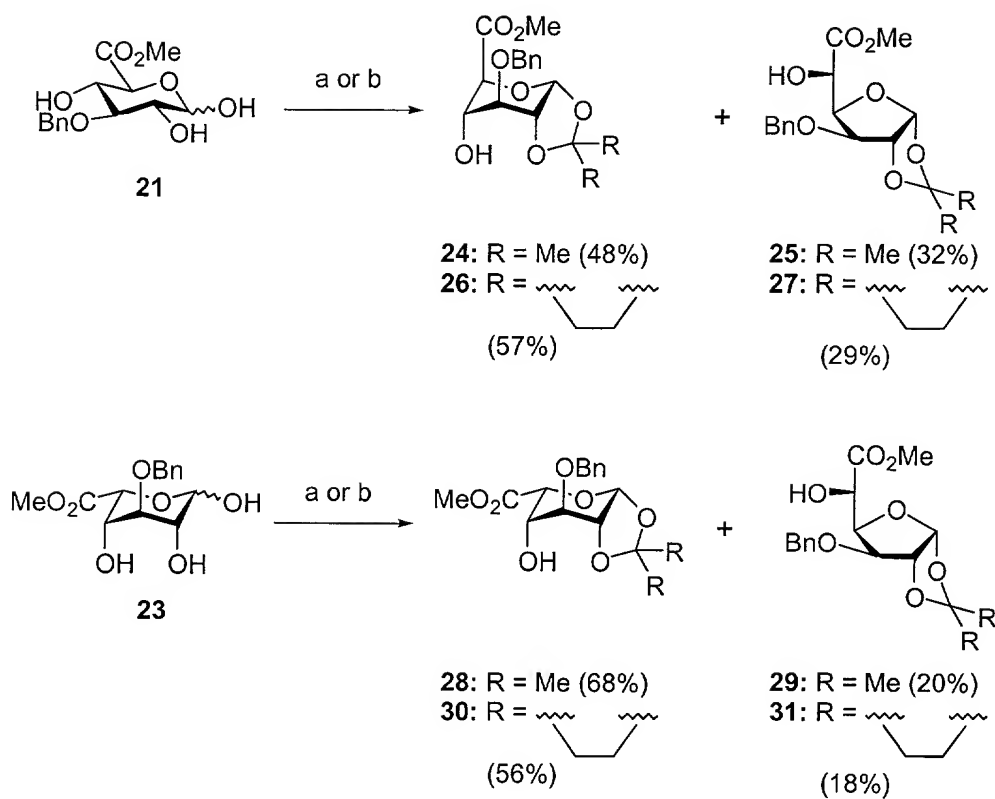
- a) 1. NaOMe, MeOH; 2. AcCl, collidine, -40°C , 93% (two steps);
 b) BnBr, Ag_2O , 4Å molecular sieves, CH_2Cl_2 , 80%;
 c) 1. THF, AcOH, TBAF; 2. CCl_3CN , DBU, CH_2Cl_2 , 88% (2 steps).

Figure 5

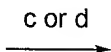


a) 1. NaH, BnBr, THF, Bu₄Ni; 2. aq. HOAc (66%), 40°C; 3. TBSCl, DMAP, CH₂Cl₂, pyridine; 4. Ac₂O, DMAP, pyridine; 5. HF-pyridine, THF; 6. TEMPO (cat.), KBr, Bu₄NBr, NaHCO₃, NaOCl, CH₂Cl₂/H₂O; 7. 4M NaOH, MeOH; 8. MeI, KHCO₃, DMF, 65% (eight steps); b) TFA (90% aq.), quant; c) 1. Tf₂O, pyridine, CH₂Cl₂; 2. LevONa, DMF, 80°C, 82% (two steps); d) N₂H₄, HOAc, pyridine, 91%.

Figure 6



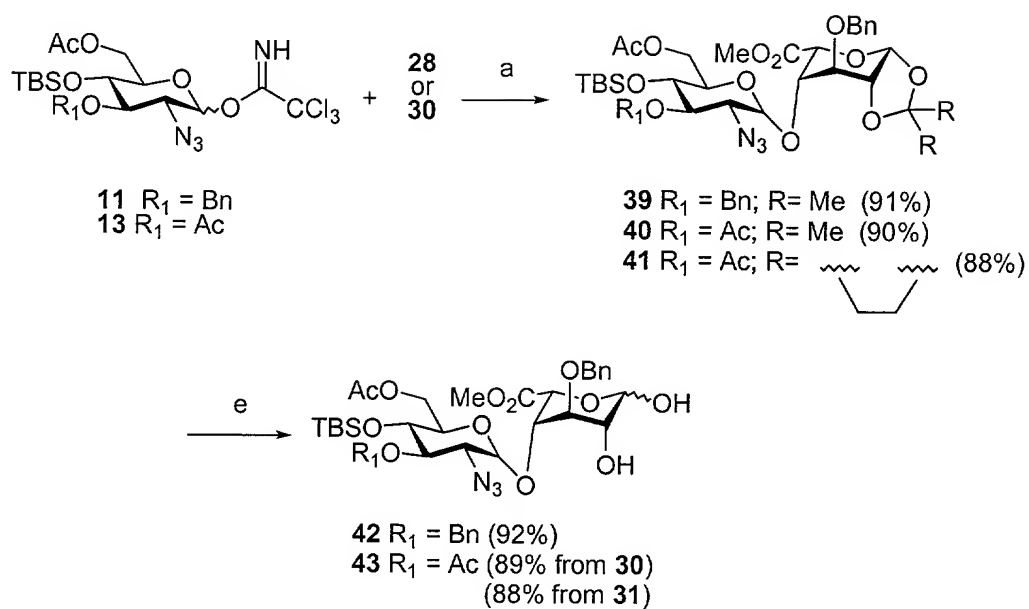
a) 2-methoxypropene, DMF, CSA;
b) methoxycyclopentene, DMF, CSA.

[illegible]

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Figure 8

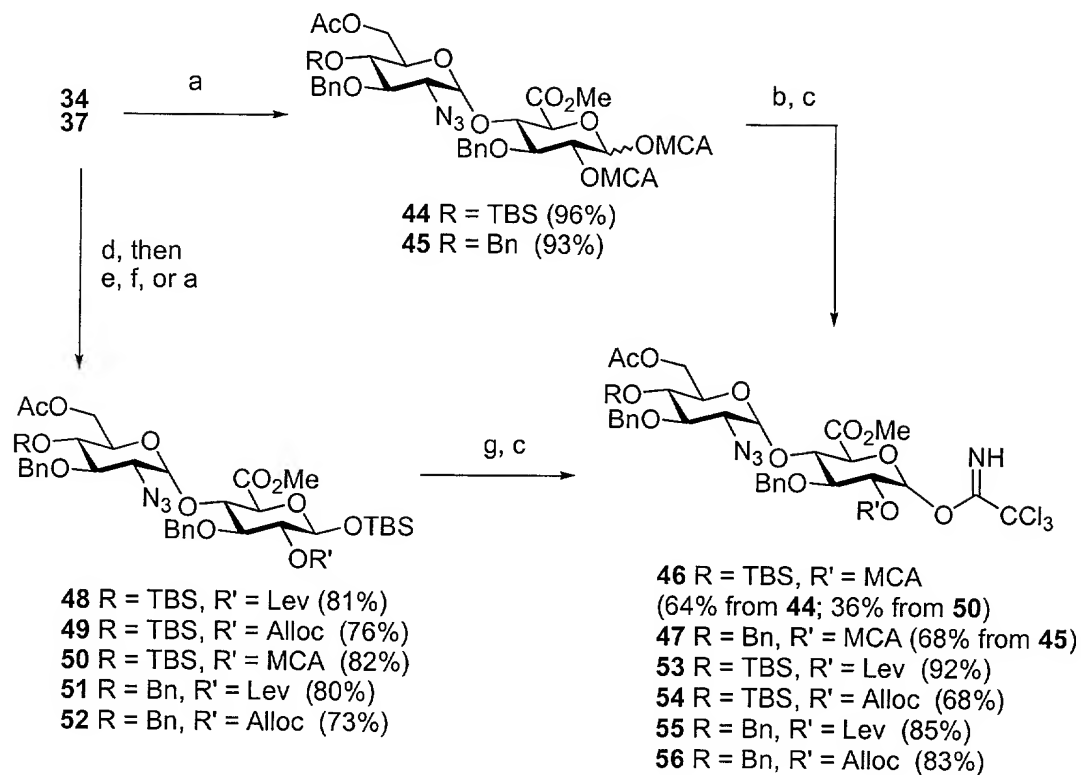
Iduronic Acid Acceptors



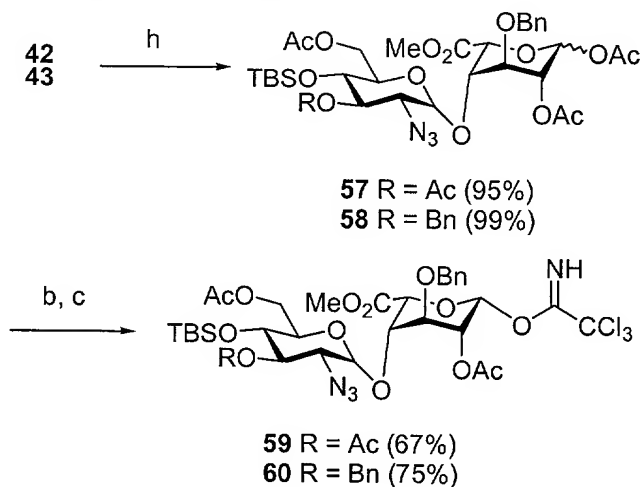
- a) TBSOTf, 4Å molecular sieves, CH_2Cl_2 , -78°C to rt;
- b) AgClO_4 , SnCl_2 , Et_2O , 4Å molecular sieves, 0°C to rt;
- c) dichloroacetic acid (75% aq.);
- d) dichloroacetic acid (50% aq.);
- e) dichloroacetic acid (60% aq.)

Figure 9

Glucuronic Acid Disaccharide Donors

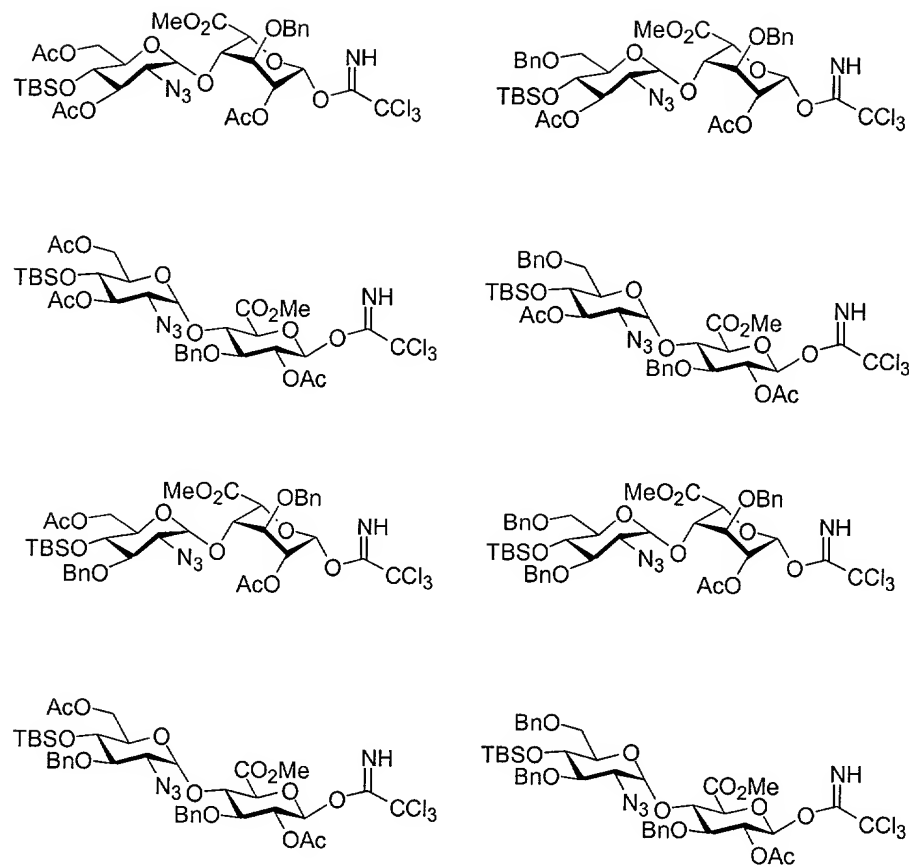


Iduronic Acid Disaccharide Donors



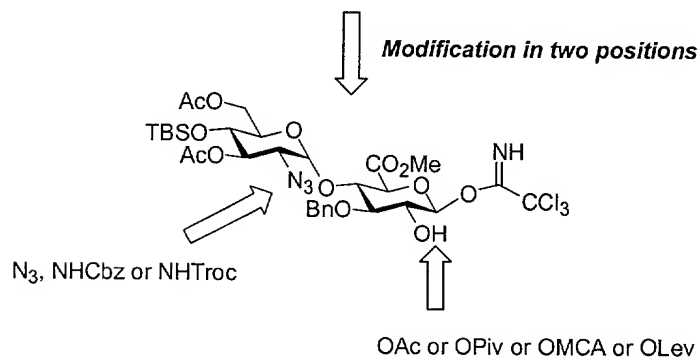
- a) (MCA)₂O, CH₂Cl₂, DMAP, pyridine; b) BnNH₂, ether, 0°C;
 c) NCCC₃, DBU, CH₂Cl₂; d) TBSCl, imidazole, CH₂Cl₂;
 e) (Lev)₂O, DMAP, CH₂Cl₂; f) AllocCl, DMAP, CH₂Cl₂;
 g) TBAF, HOAc, THF; h) Ac₂O, CH₂Cl₂, DMAP, pyridine.

Figure 10



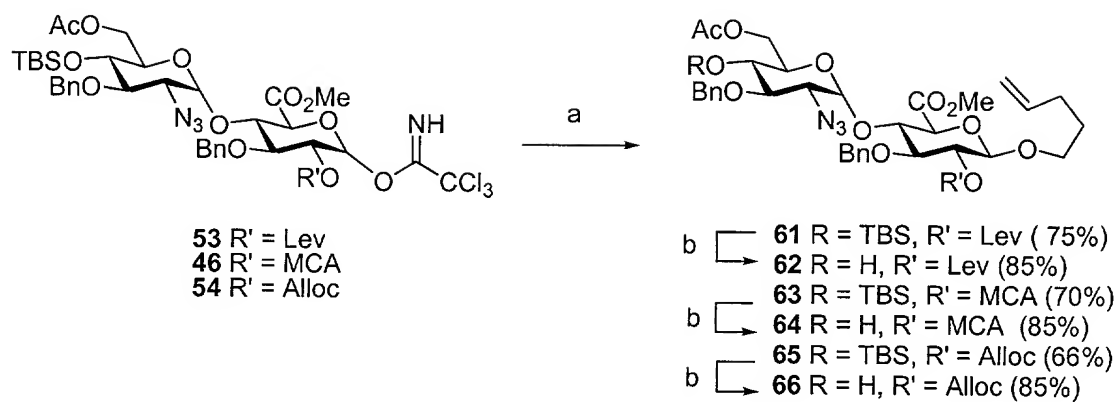
8 Disaccharide Modules

Modification in two positions



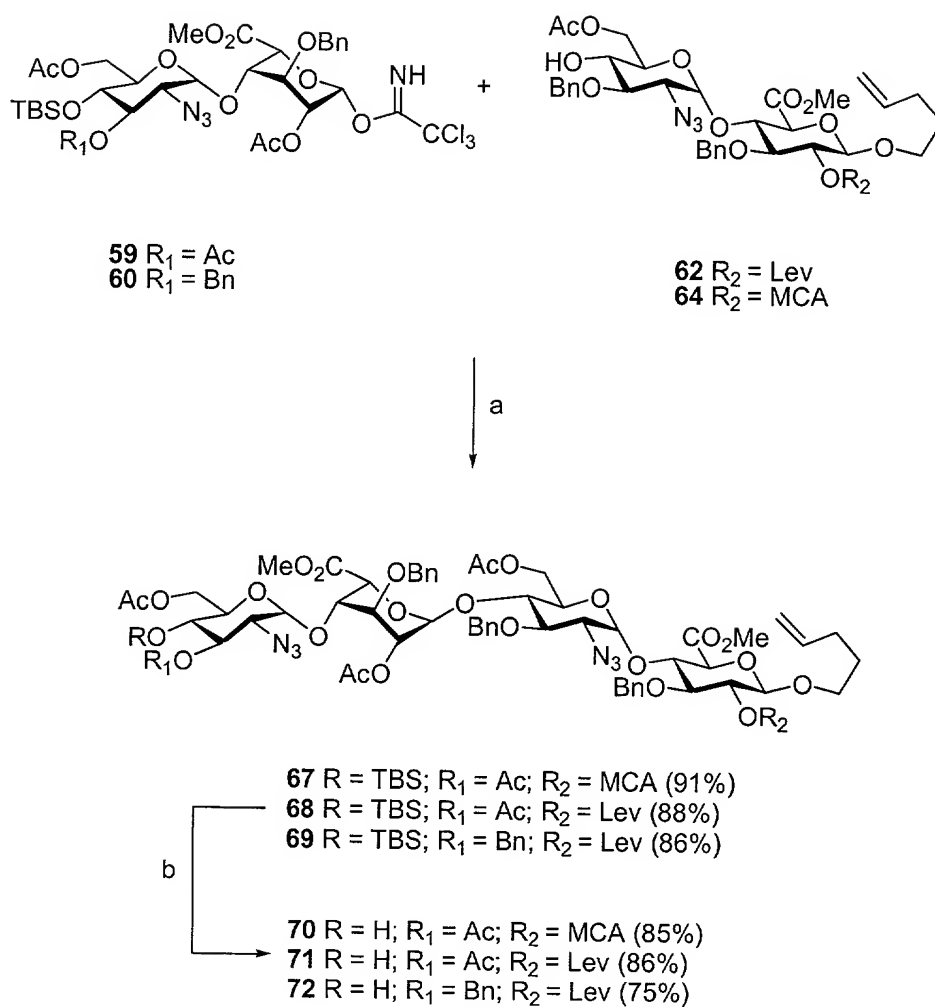
48 Disaccharide Modules

Figure 11



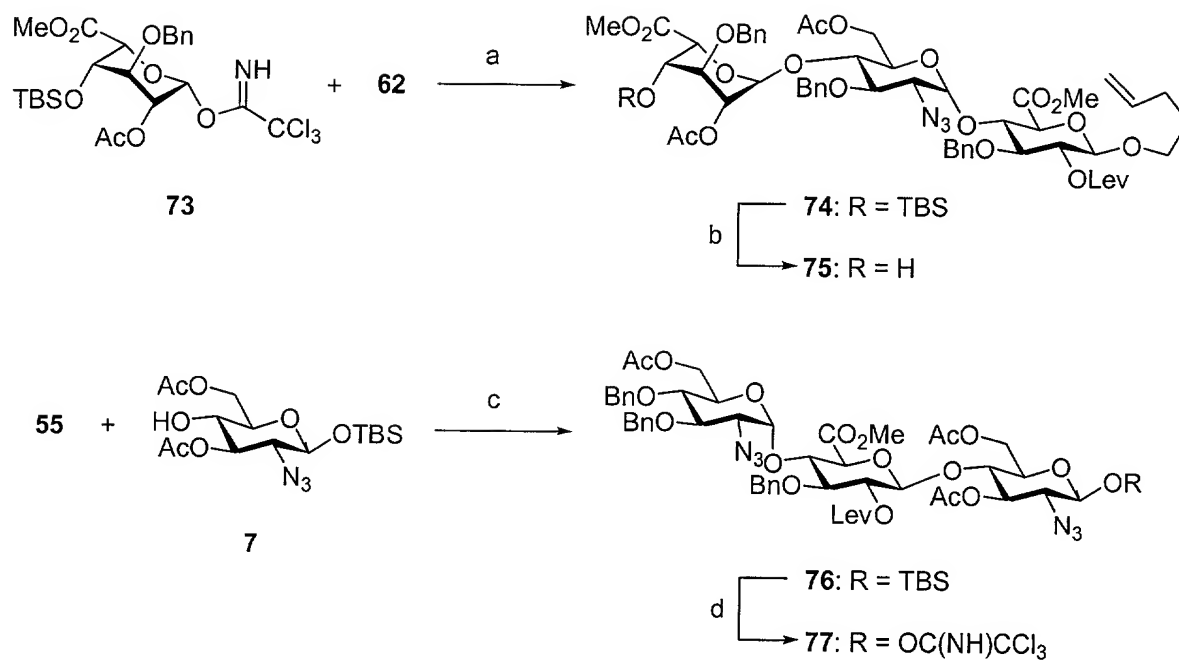
a) 4-penten-1-ol, TMSOTf, CH₂Cl₂, 0°C;
 b) HF-pyridine, HOAc, THF.

Figure 12



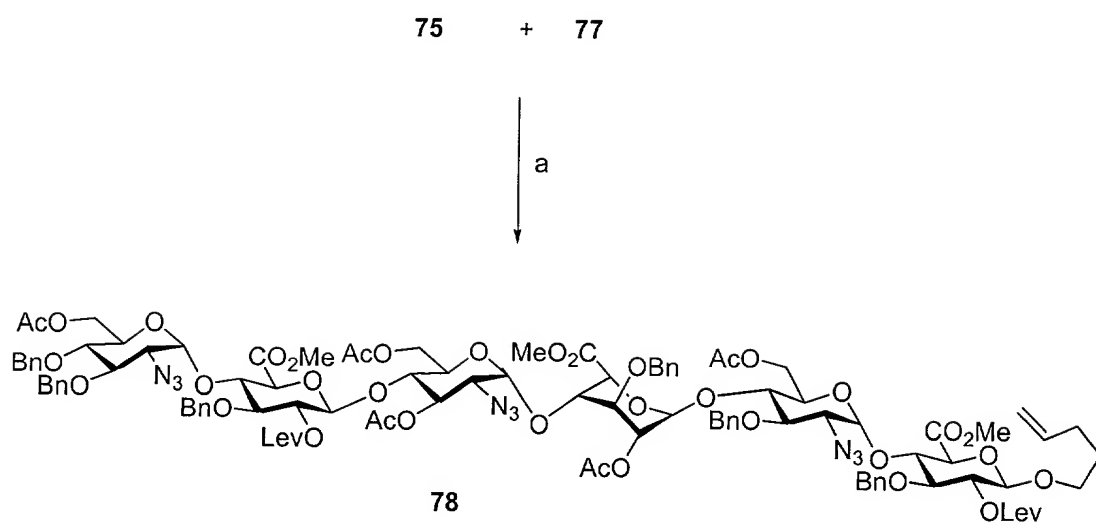
a) TMSOTf, CH_2Cl_2 , -20°C ; b) HF-pyridine, AcOH, THF.

Figure 13



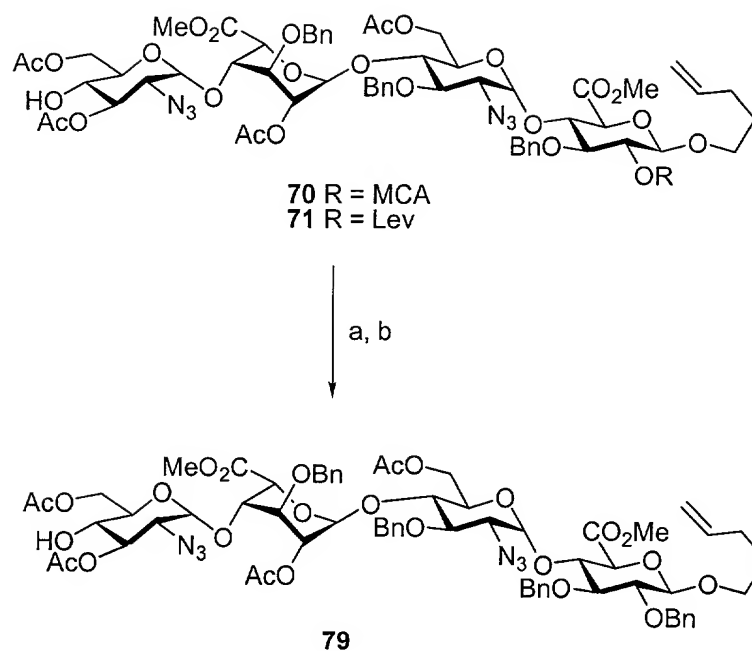
a) TMSOTf, CH₂Cl₂, -20°C, 93%; b) HF-pyridine, AcOH, THF, 82%;
 c) TMSOTf, CH₂Cl₂, -5°C, 63%; d) 1. TBAF, AcOH, THF; 2.
 Cl₃CCN, DBU, CH₂Cl₂, 0°C, 87% (2 steps).

Figure 14



a) TMSOTf, CH₂Cl₂, -20°C, 62%;

Figure 15



a) Thiourea, DMF, pyridine, rt, 24 h (90%) b) BnBr, Ag₂O, 4Å molecular sieves, CH₂Cl₂, rt, overnight (76%); c) Ac₂O, pyridine (quant.); d) NH₂NH₂-H₂O, pyridine, AcOH (90%); e) 1. aq. LiOH (0.7 M), H₂O₂ (50% aq.), THF overnight; 2. 4 M NaOH, rt overnight (82%); f) Et₃NSO₃, DMF, 50°C, overnight (50%); g) H₂, Pd/C, EtOH, water (quantitative); h) PySO₃, water (60%).

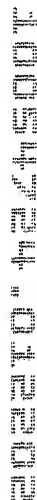


Figure 17

